



Simultaneous photodegradation of multi-herbicides by oxidized carbon nitride: performance and practical application

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ABSTRACT

This work focuses on photodegradation of multi-herbicides simultaneously with series oxidized carbon nitrides (OCN), which were synthesized via a rapid acid-assisted method. Carbon nitrides, after treating with nitric acid solution at several concentrations, revealed variant oxygen content, surface morphology and structure characteristic. The photocatalytic activity was verified by degradation of ten typical herbicides in water. The influence of microplastics on the photocatalytic performance of OCN sample was investigated for the first time. Experimental results showed that microplastics contained in environmental matrix significantly influenced the photodegradation ratio. Moreover, holes (h^+) and OH^\bullet radicals were found to be the main reactive species during this process. The OCN-10 sample demonstrated favourable reusability in recycling tests and exhibited satisfactory degradative capability for ten investigated herbicides both in soil and aqueous phase under simulated diurnal cycle.

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1. Introduction

Herbicides have been used for agricultural and industrial production persistently and heavily [1]. Their residues are detected not only in soil but in the receiving aquatic ecosystems, caused by surface runoff [2–4]. Despite of the inhibition of weeds, the active substances contained in herbicides often have negative effect on non-target organisms, following crops, human health and environment [5]. For example, acetochlor has been widely used in Europe and United States and has also been used more than 1.0×10^4 tons in China each year [6,7]. As a typical chloroacetanilide herbicide, acetochlor has been classified as possible human carcinogen and labeled as a contaminant of drinking water by the US Environmental Protection Agency [8]. Other well-known herbicides, such as diuron and nicosulfuron are trapped by long residual period or residual phytotoxicity to rotation crops, such as corn and sunflowers [9–11]. Considering the bioaccumulation and persistence, it is necessary to remove these organic micropollutants from environment.

Semiconductor based photocatalytic degradation is an effective approach to eliminate environmental contaminants [12]. Since the properties of catalysts are crucial for the photodegradation process, fabricating efficient and stable photocatalysts is the pre-requisite

[13]. Graphitic carbon nitride (GCN) has been widely studied for photocatalytic water splitting, contaminant degradation and material science because of their suitable band gap, chemical stability and low cost [14–16]. Commonly, bulk GCN is limited to the swift charge recombination and relative low visible-light utilization rate. To improve the performance of GCN, strategies including nano-structure design, heteroatom doping, hybridization and surface sensitization have been developed [17,18]. Recent reports demonstrated that doping with oxygen, which belong to higher periodic elements, is facilitative for light absorption [19–21].

In this study, series carbon nitrides with different oxygen doping degree were successfully obtained via a rapid acid-assisted approach. The photocatalytic activities of the oxidized carbon nitride (OCN) samples were evaluated by eliminating ten different herbicides, which were affiliated to five typical categories, chloroacetanilide, phenylurea, sulfonylurea, aryloxyphenoxy propanoate and triazolopyrimidine sulfonamides. The as-prepared samples showed a satisfactory degradation ratio for all investigated herbicides in water. The capacity of the optimal OCN sample was also evaluated in soil under natural light cycle. The practical photocatalytic process was affected by many factors, such as catalyst concentrations and initial pH. Besides, considering the massive plastic mulching applied in agricultural practice, and the widespread presence of microplastics in the environment [22–25], for the first, we combined this effect factor in evaluating the application potential of photocatalyst.

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Table 1
MRM transitions and other LC-MS/MS parameters of investigated herbicides.

No.	Pesticide	Retention time (min)	Confirmation transition	Quantification transition	Frag (V)
1	Acetochlor	1.824	270 → 148 (10)	270 → 224 (10)	120
2	Pretilachlor	2.745	312 → 176 (20)	312 → 252 (10)	80
3	Butachlor	3.489	312 → 162 (20)	312 → 238 (10)	80
4	Florasulam	1.011	360.2 → 192.1 (14)	360.2 → 129.1 (24)	105
5	Clodinafop-propargyl	2.650	350.2 → 238 (35)	350.2 → 266 (15)	120
6	Diuron	1.232	233 → 159.9 (30)	233 → 72.1 (20)	100
7	Nicosulfuron	0.925	411.1 → 213.3 (25)	411.1 → 182.3 (25)	135
8	Pyrazosulfuron-ethyl	1.348	415.3 → 139 (50)	415.3 → 182 (20)	140
9	Halosulfuron-methyl	1.026	435.1 → 83.2 (10)	435.1 → 182.1 (45)	135
10	Rimsulfuron	1.047	432.4 → 325.4 (25)	432.4 → 182.2 (25)	135

The collision energy (EV) is given in parentheses.

2. Material and methods

2.1. Chemicals

All chemicals used in this work were commercially available and were used without further purification. Analytical standards of ten herbicides (acetochlor, pretilachlor, butachlor, diuron, nicosulfuron, pyrazosulfuron-ethyl, halosulfuron-methyl, rimsulfuron, florasulam and clodinafop-propargyl) were provided by the Institute of the Control of Agrochemicals, Ministry of Agriculture (Beijing, China). The purities of the standard pesticides were $\geq 95\%$. Stock solutions of mixture herbicides (1000 mg L^{-1}) were prepared in acetonitrile and stored at -18°C . The working solutions were prepared daily. Doubly distilled water was used in all of the experiments.

2.2. Preparation of oxidized porous carbon nitride

Graphitic carbon nitride (GCN) was obtained by polymerization of urea at 550°C for 4 h [26]. To synthesize the oxidized carbon nitride (OCN), GCN (1.0 g) was dispersed in different concentration of HNO_3 aqueous solution (30 mL, 5.0 mol L^{-1} , 10.0 mol L^{-1} and 15.0 mol L^{-1} , respectively) and an ultrasound was then performed consecutively for 0.5 h. The initial formed suspension was centrifugal washing until neutral and the pure products were dried at 105°C for 10 h. The obtaining photocatalysts were denoted as OCN-5, OCN-10 and OCN-15, accordingly.

2.3. Characterization

A FEI Sirion 200 scanning electron microscope (SEM) was used to characterize the morphology of the synthesized samples. X-ray diffraction (XRD) patterns of the samples were recorded with a Bruker D/MAX 2500 X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) measurements were performed using an Escalab 250Xi XPS system. The specific surface areas of the samples were measured by nitrogen sorption at 77K on a Micromeritics TriStar II 3020 analyzer and calculated by the Brunauer–Emmett–Teller (BET) method. UV–vis diffuse reflectance spectra (DRS) was obtained by using a UV–Vis spectrophotometer (UV 3600, Shimadzu). For photodegradation, a 300 W xenon lamp (CEL-HFX300W, China) with cutoff filter ($\lambda > 400 \text{ nm}$) was used as the visible light source. Intelligent illumination incubator (P9X-250B, China) was used in process of simulation practical application.

2.4. Photocatalytic degradation of multi-herbicides

The photocatalytic degradation of multi-herbicides by all the CN samples was performed under visible-light ($\lambda > 400 \text{ nm}$) irradiation. All tests were carried out in a 150 mL reactor fitted with a

circulating water system to maintain a constant temperature. In a typical experiment, 100 mg photocatalysts was dispersed in 100 mL herbicides solution (2.0 mg L^{-1}) and stirred in dark to establish adsorption–desorption equilibrium between the solution and the catalysts. To study the stability of the prepared CN samples, cycling experiments were conducted. Photo catalyst was separated from the reaction solution by centrifugation (3800 rpm, 10 min) and washed with deionized water and ethonal respectively. Then it was reused in an analogous subsequent photocatalytic experiment after drying at 80°C overnight.

2.5. Analytical methods

Changes in the concentration of herbicides were determined by an Agilent 1200 HPLC series and an Agilent 6410B triple-quadrupole mass spectrometer equipped with an electrospray ionization (ESI) interface (Agilent Technologies, USA). Eclipse plus C18 column ($3.5 \mu\text{m}$ particle size, $2.1 \text{ mm} \times 50 \text{ mm}$) from Agilent Technologies was employed at 25°C . The mobile phase was $\text{H}_2\text{O}-\text{HCOOH} 0.1\%$ and acetonitrile with a flow rate of 0.2 mL min^{-1} . The triple-quadrupole mass spectrometer was operated in MRM after selected ion monitoring had been performed. Table 1 shows MRM data acquisition parameters of LC-MS/MS and additional information for the all herbicides selected (In the following figures, ten herbicides are referred to as the corresponding number for convenience).

3. Results and discussion

3.1. Characterization of the CN samples

3.1.1. Structure and morphology

The X-ray diffraction (XRD) patterns of GCN and OCN series samples are presented in Fig. 1. All samples reveal similar diffraction peaks at 12.7° (100) and 27.7° (002), corresponding to the in-plane arrangement of tri-s-triazine units and the interlayer aromatic systems stacking, respectively [27]. The typical XRD patterns indicate that the crystal structure remains untouched after oxidation treatment, which indicating the addition of oxygen atoms was achieved in a tender way. In addition, the XRD intensity of OCN samples significantly enhances compared with original GCN sample, implying an increased crystallinity of OCN series samples [28]. OCN-10 sample has shown the highest crystallinity, which is beneficial to electron diffusion [29].

The morphologies of CN samples were investigated by SEM. As shown in Fig. 2, OCN-10 exhibits the most obvious porous in the surface, while the GCN and OCN-5 samples present relatively smooth surface. Comparatively, OCN-15 sample consists of thick large particulate bulks and shows no porous feature. It seems that relative low concentration of nitric acid is hardly enough to alter the surface of GCN and form cellular structure, while overrich nitric

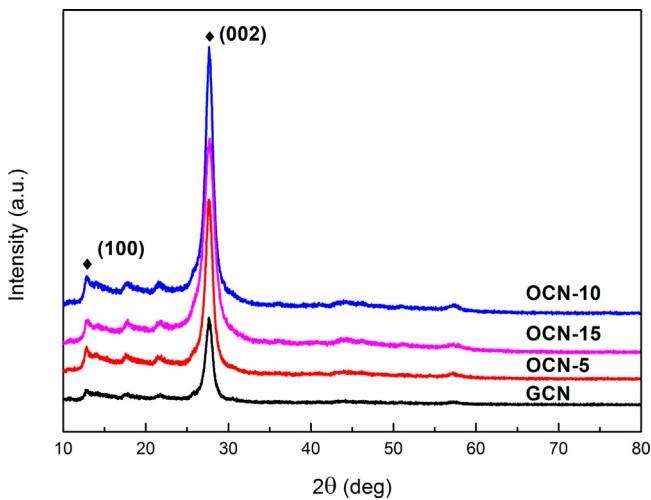


Fig. 1. XRD patterns of the prepared GCN, OCN-5, OCN-10 and OCN-15 samples.

acid may corrode the existing surface hollows and further form the cooled magma-shaped bulk. The calculated BET specific surface area of GCN, OCN-5, OCN-10 and OCN-15 samples are 59.97, 66.78, 108.94 and $23.85\text{ m}^2\text{ g}^{-1}$, respectively. The BET surface area of OCN-10 increases overtly from 59.97 to $108.94\text{ m}^2\text{ g}^{-1}$, almost twice as high as that of the GCN. Expectedly, OCN-10 also showed enlarged pore volume (Table S1), which corresponded to its porous structure observed by SEM. This specific structure ensures greater mobility of photoelectrons. Besides, the average pore diameter of OCN-10 is about 25.6 nm, which doubles the original one, indicating the increasing of mesoporous [30]. Mesoporous might bring advantage during the photodegradation process due to the convenience of diffusion and it could be easier fully accessed [31].

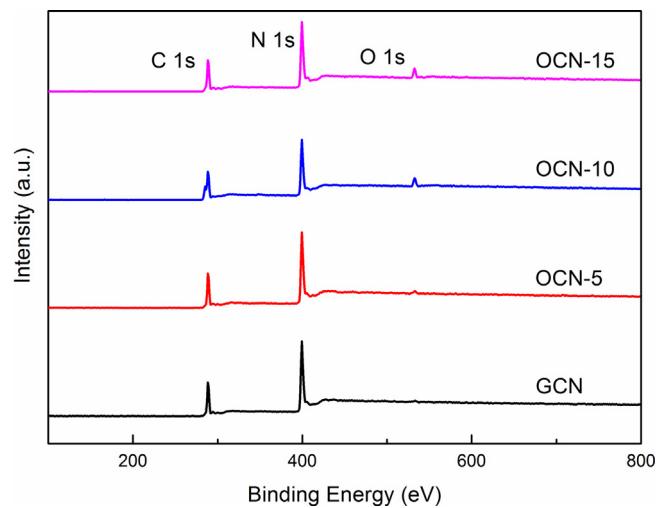


Fig. 3. The survey XPS spectra of GCN, OCN-5, OCN-10 and OCN-15 samples.

The survey X-ray photoelectron spectroscopy (XPS) was also conducted to investigate the elemental composition in CN samples. The survey scan in Fig. 3 reveals that GCN sample is based on just C and N elements, while OCN series samples are all mainly composed of C, N and O elements. And more remarkable, O element increases significantly with the increasing concentration of nitric acid. The enhancement in the deconvolution of O1s XPS of OCN samples compared with GCN further confirms the incorporation of oxygen-containing functional groups in OCN (Fig. S1). Peaks (532.2 eV, 534.4 eV) derived from oxygen adsorbed presented in pristine GCN [20]. Two additional peaks at 531.8 and 533.0 eV exhibited in three OCN samples, which correspond to C–O and nitro groups [32]. Besides, elemental analysis (EA) data of CN samples

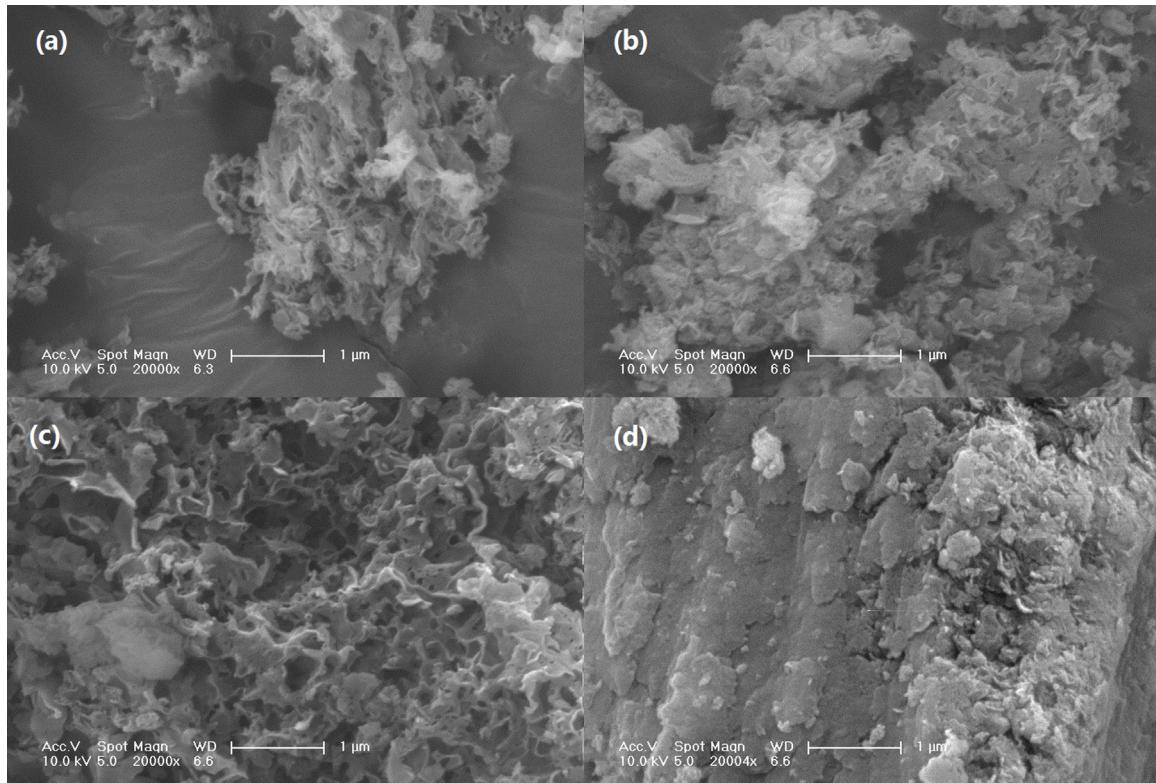


Fig. 2. SEM images of (a) GCN, (b) OCN-5, (c) OCN-10 and (d) OCN-15 photocatalyst.

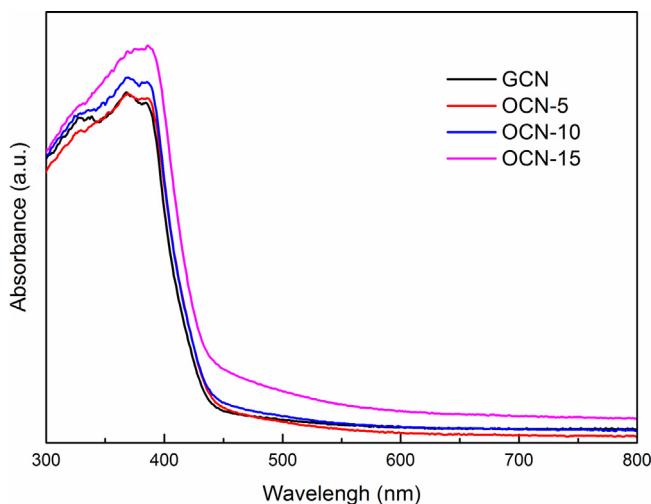


Fig. 4. The UV-vis spectra of GCN, OCN-5, OCN-10 and OCN-15.

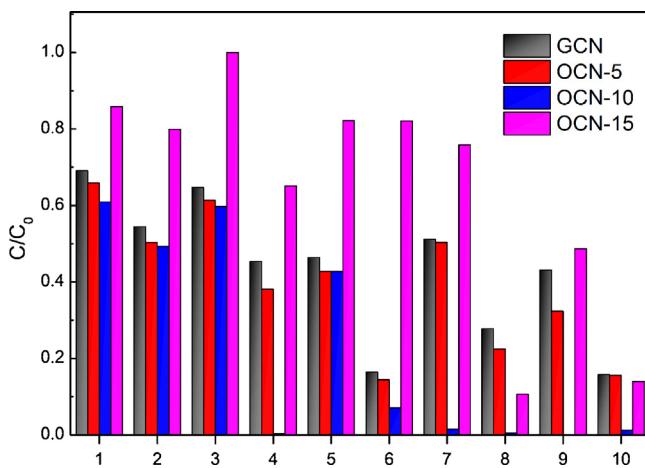


Fig. 5. Photodegradation of ten herbicides by GCN, OCN-5, OCN-10 and OCN-15 photocatalyst.

shown in Table S2 also confirmed the significant increment of O element in the prepared OCN series samples compared with GCN.

3.1.2. Optical property

The optical properties were evaluated using the UV-vis DRS spectra. As shown in Fig. 4, the as-obtained CN samples show obvious absorption from 300 to 470 nm. The intrinsic absorption edge of GCN, OCN-5, OCN-10 and OCN-15 were 450, 455, 460.5 and 469 nm and the corresponding band gaps were 2.75, 2.72, 2.69 and 2.64 eV, respectively. The adsorption intensity of OCN series sample was enhanced in different degrees in the visible region. Considering the elemental composition, the narrower band gap is corresponding to the higher oxygen content, which is coincided with previous result [33].

3.2. Photocatalytic degradation of multi-herbicides

The photocatalytic degradation of mixed herbicides over GCN, OCN-5, OCN-10 and OCN-15 catalysts are shown in Fig. 5. The degradation without photocatalyst or in the presence of photocatalyst in the dark were also tested as comparison conditions, which could be negligible under the consistent experimental. The herbicides concentration decreased significantly after irradiation for 180 min (30 min for diuron, NO. 6). For GCN, OCN-5 and OCN-10, the degradation efficiency appears to improve gradually with the

decreased optical gap. However, the OCN-15 sample reveals the lowest photocatalytic activity for most of investigated herbicides, even it possesses the narrowest band gap. For OCN-15 sample, non-radiative electron–hole recombination might become dominant, which is adverse to degradation of these herbicides [34]. Therefore, immoderate decrease in the optical gap may lead to the decreased of photocatalytic activities [14]. OCN-10 sample showed the highest photocatalytic activity. And the degradation efficiency of ten herbicides increased 3.6% to 49.6% compared to primary GCN. The advantage is more obvious in the degradation of florasulam (NO. 4) and four sulfonylurea herbicides (NO. 7–NO. 10). It is noted that, these five herbicides have similar chemical bonds ($-\text{SO}_2-\text{NH}-$). The easy degradation of herbicides NO. 4 and NO. 7–NO. 10 may due to the powerful of OCN-10 to break down the $-\text{SO}_2-\text{NH}-$ bond. Analysis for degradation products of NO. 7, 8 and 10 has further been conducted as examples, which verified the above inference (Figs. S2–S4). In spite of mediocre performance in light absorption, the distinct porous structure and increased crystallinity of OCN-10 sample may jointly promote its catalytic performance [35]. To exclude the effect of exfoliated carbon nitrides by ultrasonication during the preparation process, blank OCN-0 has been prepared in the same way with pure H_2O instead of HNO_3 aqueous solution. The degradation efficiency has been further verified by the photodegradation rate of ten herbicides. The activity of OCN-0 sample is not much difference than GCN sample. The result proved that HNO_3 indeed plays a major role during the short-time (0.5 h) ultrasonic process (Fig. S5). Above results indicate that the activity of all CN samples is complex and all related factors should be taken into account.

3.2.1. Optimization of OCN-10 dosage in aqueous suspension

To study the effect of OCN-10 dosage on the removal of mixed herbicides, the catalyst concentration was varied from 0.25 to 1.25 g L^{-1} . The initial concentration of herbicides was 2.0 mg L^{-1} for all experiments. Fig. 6 shows the effect of the catalyst dosage on 10 herbicides removal after 180 min (30 min for diuron, NO. 6) of irradiation. For three amide herbicides (acetochlor, pretilachlor and butachlor, NO. 1–NO. 3) the removal rate increased proportionally with the OCN-10 increase. But for other herbicides, the removal rate changed into decline when catalyst dosage exceeded 1.0 g L^{-1} . Therefore, all herbicides considered, the optimum value for OCN-10 is 1.0 g L^{-1} in this study.

3.2.2. Effect of initial pH

To determine the effect of pH in the removal of multi-herbicides, the initial pH of the solution was adjusted in the range from 3.0 to 11.0. The photocatalytic degradation efficiency for ten herbicides at different pH values is displayed in Fig. S6. For the entire, acidic condition plays a role in promoting the degradation. Yet, different from the system with individual contaminant, the property of all the organic pollutants in multi-component contaminant water should be assessed overall. Considering the nature of all investigated herbicides, 7.0 (natural pH) could be recommended as the most favourable pH value for the photodegradation. This implies that the application of OCN-10 catalyst does not rely on restrictive pH value.

3.2.3. Effects of microplastics

To evaluate the impact of microplastics, polystyrene (PS) particles ($<600 \mu\text{m}$) were added in the reaction system (about 10,0000 particles/ m^3). Fig. 7 presents those values. When the PS particles were added in the above system, in particular, the degradation ratio of herbicides was all restricted. This phenomenon may be due to the light absorption occurred in PS [36] and the intrinsic property of adsorption of organic pollutants [37]. Our results demonstrate that microplastic should be regarded as an impor-

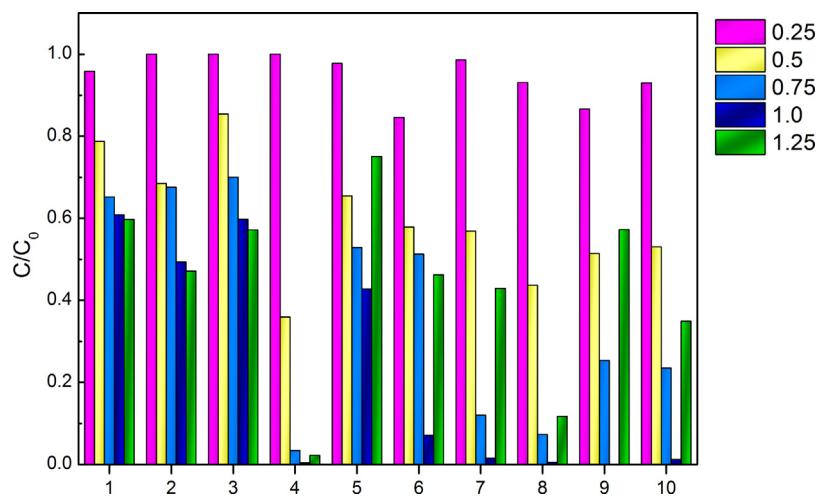
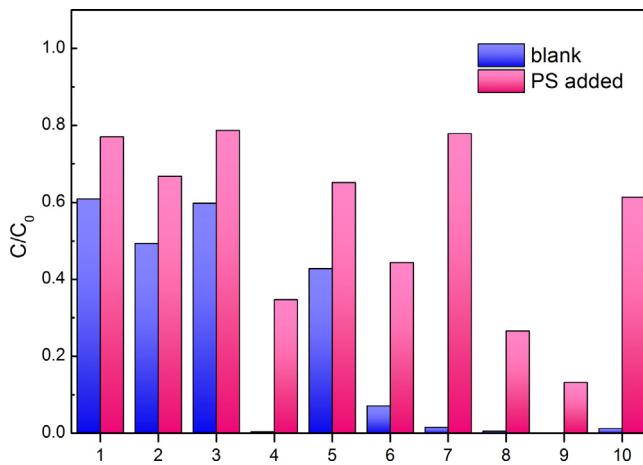


Fig. 6. Effect of OCN-10 dosage on the removal of ten herbicides.

Fig. 7. Effect of polystyrene (PS) particles in the degradation rate of 2.0 mg L^{-1} multi-herbicides in the presence of 0.1 g L^{-1} OCN-10.

tant factor in the photodegradation process of organic pollutants, especially in the practical application of catalyst.

3.2.4. Effects of different sacrificial agents

EDTA-Na₂ and tert-butyl alcohol (TBA) were selected at first to quench holes (h⁺) and •OH radicals [38,39]. Unexpectedly, EDTA-Na₂ indeed induced the change of concentration of most of the ten herbicides in the dark, possibly because it's ability for chelating with certain compounds [40]. Therefore, it cannot be used to evaluate the role of reactive species. Instead, KI was chosen as the substitution to quench holes [41]. The photodegradation efficiencies of all ten herbicides were largely inhibited by the addition of KI for all ten herbicides. Particularly, the photodegradation behaviour of amide herbicides is almost complete suppressed. Therefore, hole is the major reactive species during this process. When the TBA was added into mixed reaction solution to quench •OH radicals, the degradation showed a different pattern. For florasulam (NO. 4) and diuron (NO. 6), the photocatalytic efficiencies are almost insusceptible. The result indicates that •OH radicals are not the primary active species for these two herbicides. Besides, holes and •OH radicals play an equally important role in the degradation of butachlor (NO. 3). For other herbicides, h⁺ and •OH act together to inhibit the photocatalytic activity of OCN-10 and the influencing degree is h⁺ > •OH (Fig. S7).

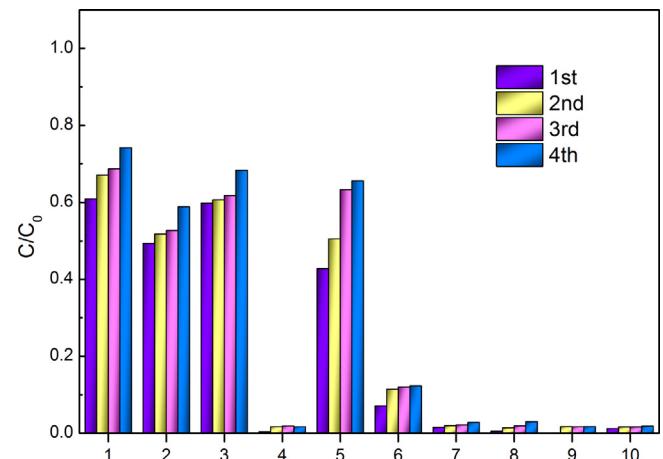


Fig. 8. The reusability of the OCN-10 photocatalyst for the reduction of multi-herbicides.

3.3. Catalyst reusability

The reusability of OCN-10 sample was tested to evaluate its practical application potentiality. As shown in Fig. 8, there is only negligible decrease of activity after four cycling runs. Due to the intrinsic stability under ambient conditions and persistent photocatalytic activity, the OCN-10 catalyst could promote to be a new candidate dealing with the environmental impact caused by herbicides.

3.4. Simulation of the practical application

In a typical experiment, 0.1 g OCN-10 was mixed with 50 mL herbicides contaminated water or 50 g contaminated soil in Petri dish. And then Petri dishes were placed in the intelligent illumination incubator (temperature 25 °C, humidity 60%, illumination intensity 1200 LX). The process of natural light cycle was simulated (photoperiod: dark/light = 12 h/12 h). The results clearly show that OCN-10 resulted in an evident decrease in herbicides concentration both in water and soil matrix under the simulated sunlight (five days). These indicate that OCN-10 catalyst is indeed a promising candidate for practical environment applications. Similarly, polystyrene (PS) particles were actually shown to restrict the photodegradation of all herbicides both in water and soil environmental (Fig. S8).

4. Conclusion

Oxygen doped carbon nitride (OCN) samples were successfully synthesized by an acid-assisted method. The concentration of dispersion medium (nitric acid) has crucial influence to the property of the catalyst. Compared to the bulk carbon nitride, the selected catalyst (OCN-10) showed the highest photocatalytic activity for all investigated herbicides, which is due to the enlarged specific surface area, higher crystallinity and the narrower band gap which ascribed to the appropriate oxygen intervention. Also, the effect of microplastics during photocatalytic process has been considered, which is instructive to inspect the application prospect of catalyst candidates. This work implies promising applications of the selected oxidized carbon nitride photocatalyst in remediating contaminative soil and water under actual daylight.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.07.007>.

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